The Colour of Gold and its Alloys

THE MECHANISM OF VARIATION IN OPTICAL PROPERTIES

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The optical properties of metals, and particularly their high reflectivity, are related to the effect on their free electrons of the energy of the incident light, but a satisfactory explanation of the characteristic colours of gold and its alloys and intermetallic phases has become possible only since calculations could be made of energy band structures.

Although there has been a continued interest in the colours of gold and gold alloys from the times of ancient Egypt onwards, our knowledge of the causes and mechanisms responsible for the optical properties of metals and alloys is of relatively recent origin. The assumption of the existence of free conduction electrons in metals gives the basis for a qualitative explanation of the generally high reflectivity of an untarnished metal surface. A more sophisticated approach, however, is necessary in order to understand the reason for the colouration of metals like gold and copper, or for the greyish tinge exhibited by metals like nickel, palladium or platinum.

The colour of an opaque body is governed by the dependence of its reflectivity upon the frequency, or the energy, of the incident light. Thus a material possessing a much higher reflectivity for the low energy end of the visible spectrum (red and yellow light) than for the other parts of the spectrum will have a reddish to yellow colour. In the case of materials with metallic properties, a satisfactory interpretation of this dependence of reflectivity on the energy of incident light has only become possible since calculations of the energy band structure could be made. For most of the pure metals, a number of intermetallic phases, and a few dilute alloys, fairly detailed band calculations are available. Less progress has been made with alloys containing substantial amounts of alloying additions. Nevertheless, a certain amount of insight into the mechanisms responsible for colour variations can be gained from our knowledge of the changes in band structure due to alloying as found from the studies on non-optical properties which also depend on electron band structure.

The rich yellow colour of gold is caused by the pronounced step in the reflectivity curve at an energy of incident light of approximately 2.3 eV, as shown in Figure 1, curve 1. The decrease in reflectivity from the high values characteristic for free electrons is due to the fact that absorption processes set in at energies in the vicinity of 2 eV. Absorption processes in metals are made possible by band transitions, that is by transitions of electrons from the conduction band to energetically higher bands, or transitions from lower bands to energy states of the conduction band which are situated above the Fermi level. According to the selection rules required by group theory, only part of the energetically possible transitions are permitted in the perfect crystal. In real crystals, however, these selection rules are of only limited validity because of the high density of lattice defects normally present. Of material importance for the intensity of the absorption process is the density of states in the electron bands involved in the transition. Thus it can happen that a band transition is both energetically possible and permitted by the selection rules but does not yield an appreciable adsorption process because the relevant densities of state are low.

In the case of gold all the conditions for an intense absorption process at about 2.3 eV are met by a transition from a d-band to unoccupied states in the conduction band. It can be concluded then, that the yellow colour of fine gold is ultimately due to this electron transition. With copper, whose electronic structure is quite similar to that of gold, a corresponding transition at slightly lower energies is responsible for its red colour. The electronic structure of silver is also very similar to that of gold, but here the d-bands are situated so far below the Fermi level that the corresponding transition requires an energy in excess of that of the violet end of the visible spectrum. Thus the high reflectivity due to the free

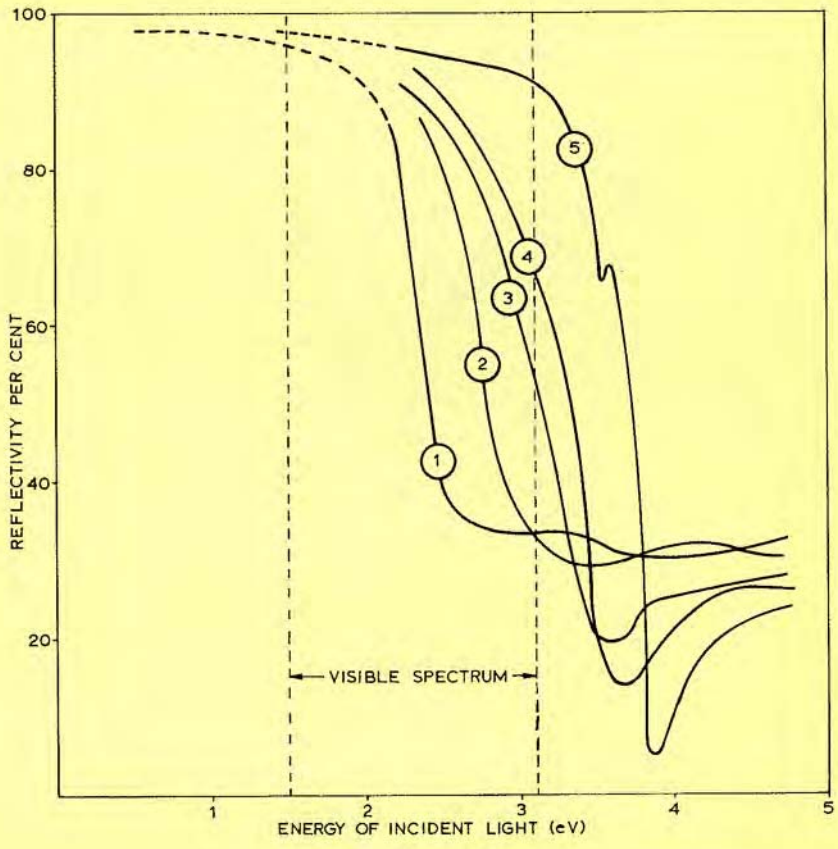

Fig. 1 Reflectivity as a function of the energy of incident light for gold, silver and three of their alloys (after Fukutani and Sueoka)

Curve 1 Fine gold

Curve 2 Silver with 50 atomic per cent gold

Curve 3 Silver with 10 atomic per cent gold

Curve 4 Silver with 5 atomic per cent gold

Curve 5 Fine Silver

The rich yellow colour of gold is caused by the pronounced step in the reflectivity curve at an energy of incident light of approximately 2.3 eV. As the silver content is progressively increased the slope of the reflectivity curve is shifted towards higher energies. Thus not only the red and yellow regions of the spectrum, but also the green region are strongly reflected at medium silver contents. At higher silver contents the reflectivity edge has moved so far into the blue and violet regions that almost the whole of the visible spectrum is reflected and the alloys assume a white colour

electron gas is maintained over the whole extent of the visible spectrum, and this is the reason why silver is a pure white.

From the facts outlined above it becomes possible to understand the changes in colour in the gold-silver alloy system. As gold and silver are quite similar in their electronic structures it can be expected that the band structure as such will be preserved throughout the alloy system. With the addition of silver to gold, however, the energy gap between the d-bands and the Fermi level, which is decisive for the band transitions that govern the colour, is continuously widened. Thus the point at which the drop in reflectivity occurs is shifted towards higher energies, while the height of the step and the steepness of the slope remain roughly the same. This can be seen quite clearly from the experimental data reported, for instance, by Köster and Stahl (1) or by Fukutani and Sueoka (2), again shown in Figure 1. As a result of this shift of the reflectivity edge, not only the red and the yellow regions of the visible spectrum, but also the green region, are strongly reflected at medium silver contents, the reason for the greenish tinge of these alloys. As the silver content is progressively increased, the reflectivity edge is shifted so far into the blue and violet regions that practically the whole of the visible spectrum is strongly reflected, and the alloys containing more than 70 atomic per cent (56 weight per cent) silver assume a more or less white colour.

For the case of the decolourising effect of additions of nickel or palladium to gold, the notion of a continuous shift of the relevant band gaps, as described above, cannot be applied. The reflectivity curves determined by the authors (3) for the two alloy systems gold-nickel and gold-palladium—shown in Figures 2 and 3—make this quite obvious. Here a different interpretation has to be looked for. It is found by assuming that, when monovalent noble metals are alloyed with transition metals like nickel or palladium, so-called "virtually bound states" will occur. This notion was first suggested by Friedel (4). It can be compared with the reasonance effect of classical mechanics as found for two coupled vibrating systems with very similar natural frequencies. As Abelès (5, 6) was able to show, the maxima of the relatively broad absorption peaks caused by these virtually bound states lie at energies of about 0.8 eV for Au-Ni and 1.7 eV for Au-Pd. This means that, by adding nickel or palladium to gold, absorption processes become possible at energies considerably below those necessary for the occurrence of absorption

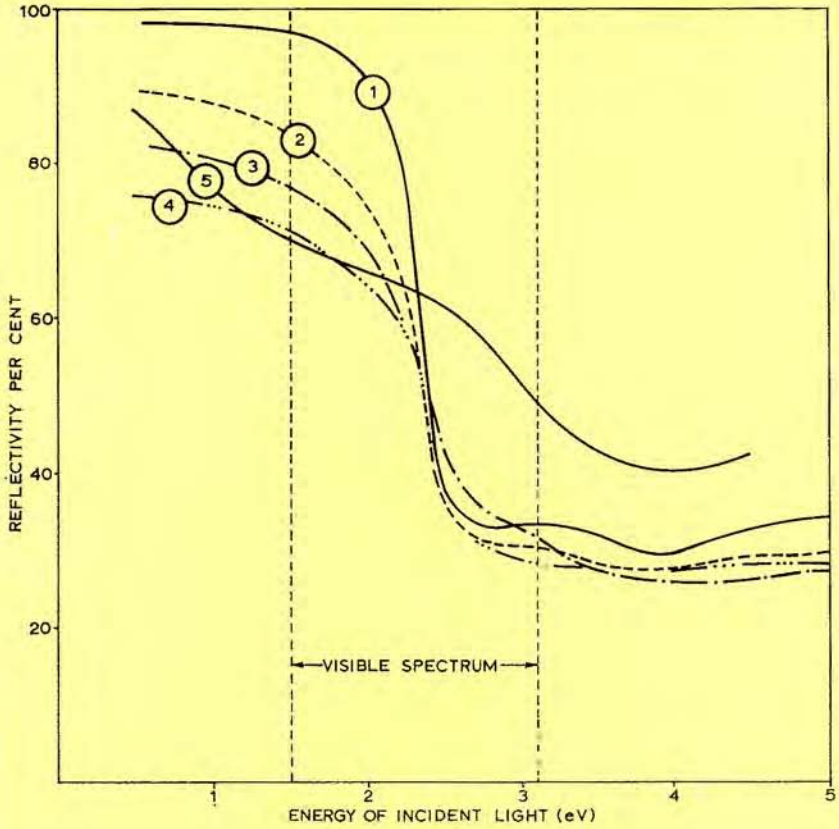

Fig. 2 Reflectivity as a function of the energy of incident light for some gold-nickel alloys as determined by the authors (3)

Curve 1 Fine gold

Curve 2 Gold with 2 atomic per cent nickel

Curve 3 Gold with 5 atomic per cent nickel

Curve 4 Gold with 10 atomic per cent nickel

Curve 5 Pure nickel

The step in the reflectivity curve responsible for the yellow colour of gold becomes less pronounced with additions of nickel, the reflectivity being reduced for the low energy parts of the visible spectrum

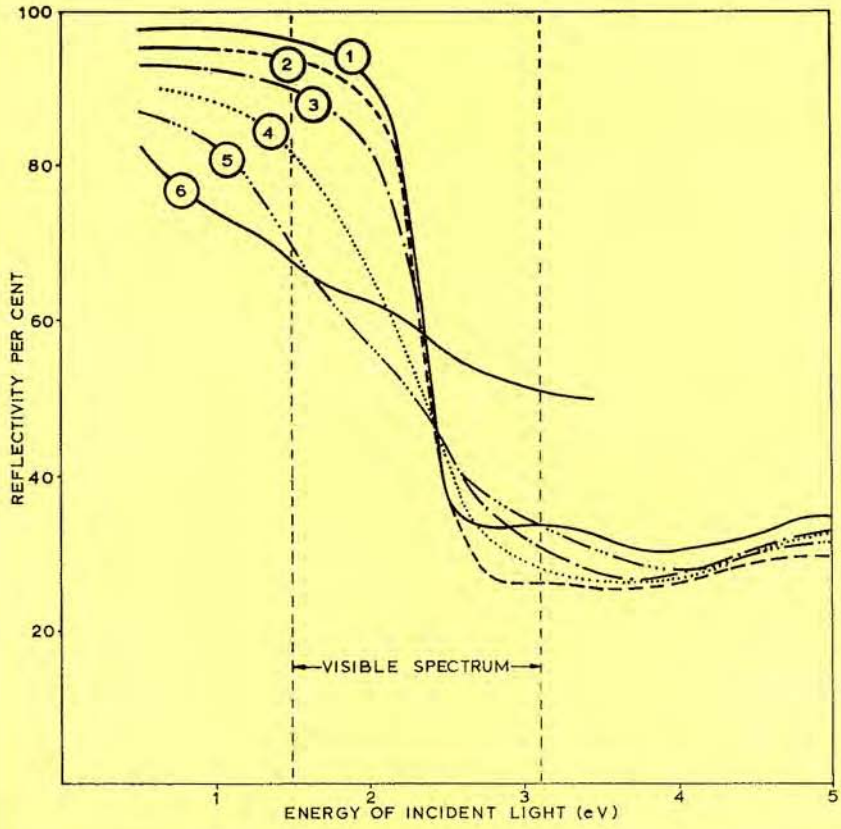

Fig. 3 Reflectivity as a function of the energy of incident light for some gold-palladium alloys (3)

Curve 1 Fine gold

Curve 2 Gold with 5 atomic per cent palladium

Curve 3 Gold with 10 atomic per cent palladium

Curve 4 Gold with 20 atomic per cent palladium

Curve 5 Gold with 30 atomic per cent palladium

Curve 6 Pure palladium

As with the gold-nickel alloys, absorption processes become possible at energies considerably below those characteristic of pure gold and the reflectivity is reduced in the red and infra-red regions of the spectrum

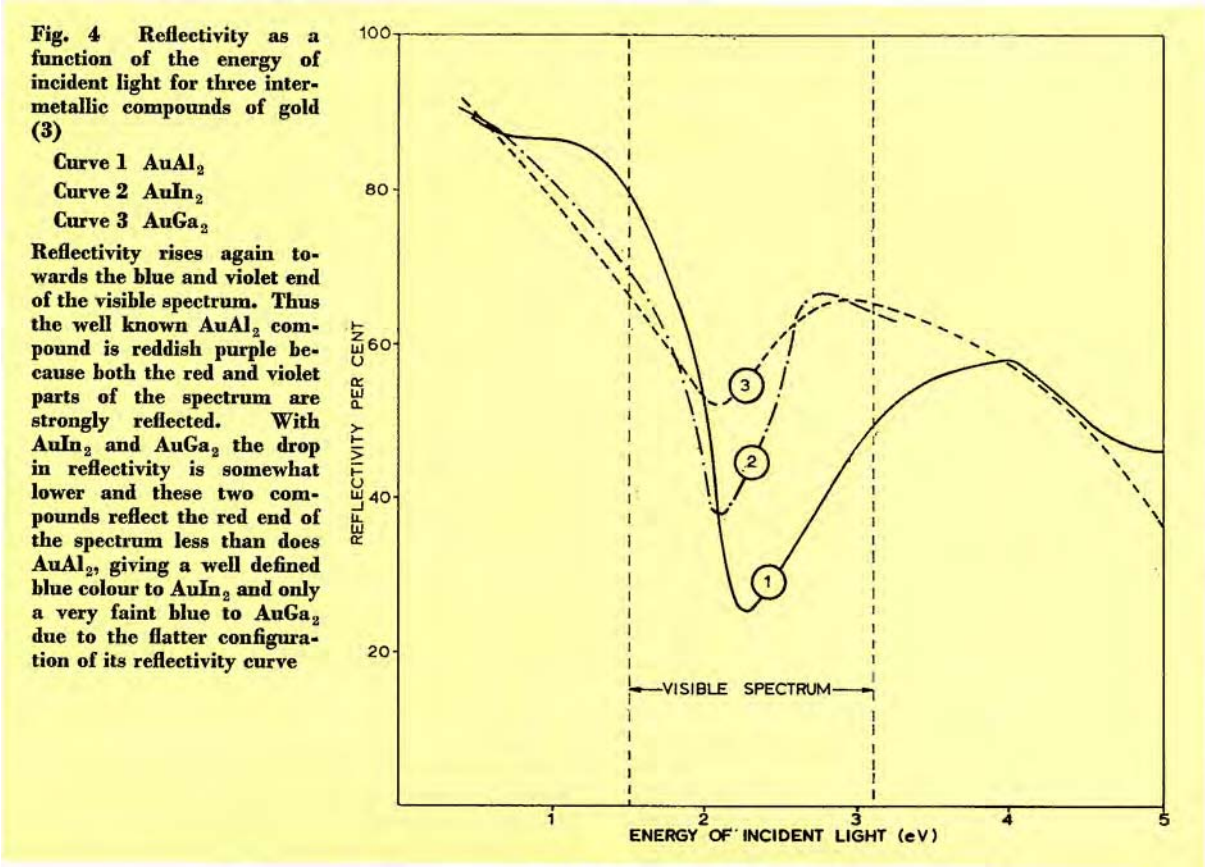

Fig. 4 Reflectivity as a function of the energy of incident light for three intermetallic compounds of gold (3)

Curve 1 $AuAl_2$
Curve 2 $AuIn_2$
Curve 3 $AuGa_2$

Reflectivity rises again towards the blue and violet end of the visible spectrum. Thus the well known $AuAl_2$ compound is reddish purple because both the red and violet parts of the spectrum are strongly reflected. With $AuIn_2$ and $AuGa_2$ the drop in reflectivity is somewhat lower and these two compounds reflect the red end of the spectrum less than does $AuAl_2$, giving a well defined blue colour to $AuIn_2$ and only a very faint blue to $AuGa_2$ due to the flatter configuration of its reflectivity curve

processes in pure gold. Thus the reflectivity of these alloys is markedly decreased already in the infra-red and red regions of the spectrum. As a result the step in the reflectivity curve which is responsible for the yellow colour of fine gold becomes less pronounced. In other words, the decolourising effect of nickel or palladium is brought about by lowering the reflectivity for the low energy part of the visible spectrum. The energy for the transitions due to the virtually bound states remains practically unaffected by the quantity of the alloying addition, only the intensity of the absorption process being changed (6). This mechanism, i.e., the superposition of two absorption peaks, explains why the slope of the reflectivity curve is flattened and why the curve itself is not shifted in a significant manner as it is in the case of the gold-silver alloys.

For both these groups of alloys the alloys of gold with palladium or nickel on the one hand and the gold-silver alloys on the other, it was possible to base the interpretation of the experimental data on the reflectivity curve of pure gold. This is not so for the alloys of gold with 66.6 atomic per cent aluminium, gallium, and indium respectively, as these alloys form intermetallic phases. In the case of the formation of an intermetallic phase an entirely new band structure is produced which normally does not bear any resemblance to the band structures of its constituents. However, as intermetallic phases in some ways behave like pure metals, band structure calculations can be carried out for them. For the three intermetallics concerned, $AuAl_2$, $AuGa_2$, and $AuIn_2$, which are quite similar in electronic and crystal structure, this was done by Switendick and Narath (7). From their calculations it is seen that with $AuAl_2$ band transitions from the Fermi level to unoccupied states of higher energy bands are possible at an energy of about 2.1 eV. The energy range within which these transitions can occur is relatively narrow. As a result of this the reflectivity rises again towards the violet end of the visible spectrum, as may be seen in Figure 4, curve 1. With both the red and the violet regions being much more strongly reflected than the green and yellow parts of the spectrum this alloy exhibits a striking reddish-purple colour.

For $AuGa_2$ and $AuIn_2$ the energies of the corresponding transitions are somewhat lower, and the related minima in the respective reflectivity curves are shifted accordingly. For this reason the red part of the spectrum is reflected considerably less strongly by $AuIn_2$ and $AuGa_2$ than it is by $AuAl_2$, and the reflectivity is higher for blue and violet light. From this results a clear blue colour for $AuIn_2$ and a slight

bluish hue for $AuGa_2$. It is interesting that the energies for the respective minima and maxima in the reflectivity curves are quite similar for the two compounds, $AuIn_2$ and $AuGa_2$. The distinct difference in the intensity of their colouration is to be attributed to the fact that the differences in reflectivity for the various regions of the visible spectrum are less strongly pronounced with $AuGa_2$ than with $AuIn_2$. This, in turn, may be taken as an indication that the densities of state for the energy bands involved in the transition described above differ considerably for these two alloys.

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